Studies of the Organic Reactions of Metal Carbonyl. IV. The Acceleration Effect of the Addition of Organic Compounds on the Reaction of Olefin Oxide with Cobalt Hydrocarbonyl and on the Hydroformylation of Olefin Oxide

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It has been demonstrated elsewhere[1,2] that olefin oxides react with cobalt hydrocarbonyl and carbon monoxide to form β-hydroxyacylcobalt carbonyls which can be converted to the corresponding esters of β-hydroxycarboxylic acid by cleavage with iodine and alcohol. On the other hand, the present authors have recently reported[3] that propylene oxide undergoes hydroformylation to form β-hydroxy-*n*-butyraldehyde as the major product.

The authors have found that the alcohol used in the cleavage reaction has an acceleration effect on the reaction of olefin oxide with cobalt hydrocarbonyl. The present investigation has aimed at examining in detail the effect of the addition of various organic compounds on these types of reaction. The results described in this paper indicate that some organic compounds, such as alcohol, ketone, ether and ester, accelerate remarkably the reaction of olefin oxide with cobalt hydrocarbonyl. A similar effect has been also observed in the hydroformylation of olefin oxide.

Experimental

Reaction Procedures.—The reactions of olefin oxide with cobalt hydrocarbonyl were carried out in the way described in a previous paper[2] using 50 ml. of a 0.09 M cobalt hydrocarbonyl solution in toluene. Various amounts of organic compounds were added at the beginning or during the reaction.

The hydroformylation of olefin oxide was investigated, in the manner which has been described previously,[3] in the presence of ethyl alcohol using dicobalt octacarbonyl as a catalyst.

Analytical Procedures.—The reaction products were analyzed by gas chromatography and by means of infrared spectra which had been taken on a Shimadzu model IR-27 infracord spectrophotometer. The details were given in previous papers.[2,3] The hydroformylation product of ethylene oxide was isolated as 2,4-dinitrophenylhydrazone and recrystallized from chloroform.

Meterials.—Ethylene oxide, propylene oxide, styrene oxide, epichlorohydrin and the other organic compounds employed in this study were commercial products, all of which were proved to be sufficiently pure by gas chromatography.

Results and Discussion

The Reactions of Propylene Oxide with Cobalt Hydrocarbonyl in the Presence of Various Organic Compounds.—All reactions were carried out at the mole ratio[*1] of 1.6, at which the reaction without additives proceeds very slowly.[2] The results of the reactions in the presence of ethyl alcohol are summarized in Table I and in Figs. 1, 2 and 3. In Fig. 1 the amounts of carbon monoxide absorbed at 0°C are plotted against the reaction time. These gas absorption curves indicate a remarkable increase of the reaction rate upon the addition of a relatively small amount of ethyl alcohol. Without the additive (curve A),

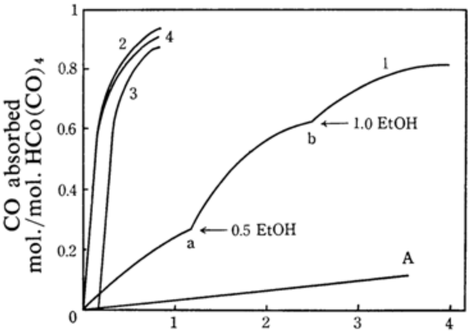

Fig. 1. CO absorption vs. time plots for the reactions of propylene oxide in the presence of ethyl alcohol at 0°C.
A: without ethyl alcohol
Numbers (1—4) correspond with Exp. No. in Table I.
a and b: At these points, 0.5 and 1.0 mol. of ethyl alcohol were added, respectively.

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1) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1460 (1963).

2) Y. Takegami, C. Yokokawa. Y. Watanabe and H. Masada, This Bulletin, **37**, 672 (1964).

3) C. Yokokawa, Y. Watanabe and Y. Takegami, ibid., **37**, 677 (1964).

[*1] Mole of propylene oxide per mole of cobalt hydrocarbonyl used.

TABLE I. THE REACTION OF PROPYLENE OXIDE WITH COBALT HYDROCARBONYL IN THE PRESENCE OF ETHYL ALCOHOL

Exp. No.	Reaction condition[*1]		EtOH added (mol./mol.-$HCo(CO)_4$)	CO absorbed (mol./mol.-$HCo(CO)_4$)	Product (mol./mol.-$HCo(CO)_4$)	
	Temp. °C	Time min.			Ester[*2]	Aldehyde[*3]
1	0	250	0.5+1.5[*4]	0.80	0.34	—
2	0	50	2.0	0.93	0.49	—
3	0	50	3.0	0.88	0.47	—
4	0	80	4.0	0.87	0.40	0.05
5	−30	155	2.0	0.93	0.55	—
6	−30	170	2.0	0.82	0.53	—
7	−30	110	3.0	0.72	0.52	—
8	−45	220	1.0	0.88	0.66	—
9	−45	230	2.0+2.0[*4]	0.89	0.64	0.05
10	−45	90	2.0	0.62	0.48	—
11	−55	330	2.0	0.82	0.63	—
12[*5]	0	100	2.0	0.90	0.24	—
13[*5]	−45	265	2.0+2.0[*4]	0.94	0.59	—

[*1] Under one atmosphere of carbon monoxide and 1.6 mol. ratio of propylene oxide The speed of stirring was 900 r. p. m.
[*2] Ethyl β-hydroxy-*n*-butyrate
[*3] β-Hydroxy-*n*-butyraldehyde
[*4] Added during the reaction
[*5] In *n*-heptane solvent

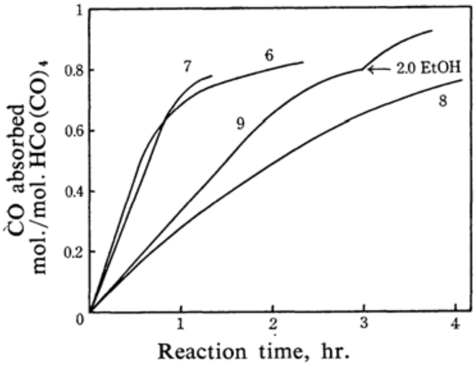

Fig. 2. CO absorption vs. time plots for the reactions of propylene oxide in the presence of ethyl alcohol at −30 and −45°C.

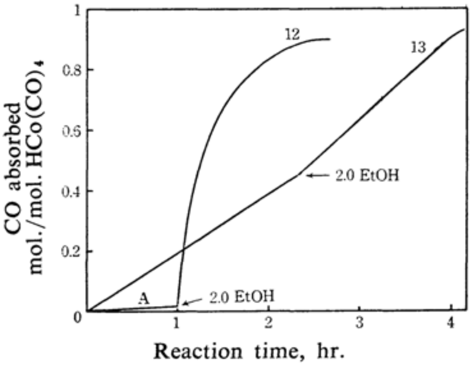

Fig. 3. CO absorption vs. time plots for the reactions of propylene oxide in *n*-heptane.
A: without ethyl alcohol

only 0.1 mol.[*2] of the gas was absorbed in three hours. When 0.5 mol.[*3] of the alcohol was added (Exp. 1 and curve 1), 0.3 mol. of the gas was absorbed in 70 min. Additional amounts of the alcohol (0.5 and 1.0 mol.) also promoted the gas absorption. By the addition of 2.0 mol. of the alcohol (Exp. 2) in the beginning, the rate of the gas absorption was about one hundred and twenty times larger than that of the standard run. The increase in the rate of the gas absorption with the increase in the amount of the alcohol added seemed to cease, however, at the amount of 2.0 mol. since the rates of Exps. 3 and 4 (3.0 and 4.0 of the alcohol were added respectively) were comparable to that of Exp. 2. No gas absorption was observed in the systems of cobalt hydrocarbonyl and ethyl alcohol or of propylene oxide and ethyl alcohol.

The main product in these reactions was ethyl β-hydroxy-*n*-butyrate.[*4] In addition to this ester and a small amount of β-hydroxy-*n*-butyraldehyde, there was no indication of the presence of other product in the gas chromatogram. The total yield of the ester and aldehyde, based on the amount of gas absorbed, is about 50% almost the same as that of the reactions without the alcohol.[2)]

The acceleration effect of the alcohol was also observed at −30 and −45°C, as Fig. 2

[*2,*3] Mole per mole of cobalt hydrocarbonyl used.
[*4] This compound can be obtained from the corresponding acylcobalt carbonyl by cleavage with iodine and ethyl alcohol.[2)]

TABLE II. THE REACTION OF PROPYLENE OXIDE WITH COBALT HYDROCARBONYL IN THE PRESENCE OF VARIOUS KINDS OF ORGANIC COMPOUND

Exp. No.	Reaction*1 time min.	Compound added		CO absorbed (mol./mol.-$HCo(CO)_4$))	Relative absorption rate*2	Product Ester*3 (mol./mol.-$HCo(CO)_4$)
		Name	(mol./mol.-$HCo(CO)_4$)			
A	180	None	—	0.10	1	—
14	90	Ethyl alcohol	2.0	0.93	120	0.45
15	210	Ethylene chlorohydrin	2.0	0.81	10	—
16	35	*n*-Butyl alcohol	3.0	0.87	120	0.48*4
17	40	*t*-Butyl alcohol	3.0	0.53	120	0.32
18	180	Acetone	3.0	0.70	25	0.33
19	240	Chloroacetone	3.0	0.73	9	—
20	270	Acetylacetone	3.0	0.81	14	0.40
21	150	Acetophenone	2.0	0.49	12	0.29
22	265	Ethyl ether	2.0+2.0+2.0	0.71	6	0.43
23	180	Tetrahydrofuran	3.0	0.71	30	—
24	270	Acetal	3.0	0.86	17	0.42
25	210	Benzaldehyde	3.0	0.64	9	—
26	210	Ethyl acetate	3.0	0.86	12	0.42
27	180	Acetonitrile	3.0	0.61	12	0.43
28	50	Nitromethane	3.0	0.06	1~2	—
29	60	Phenol	2.0	0	—	—

*1 Other reaction conditions : under one atmosphere of carbon monoxide, at 0°C and at 1.6 mol. ratio of propylene oxide

*2 The relative value of the absorption rate at the early stage of the reaction to the rate of Exp. A

*3 Ethyl β-hydroxy-*n*-butyrate

*4 Ethyl β-hydroxy-*n*-butyrate 0.40 and *n*-butyl β-hydroxy-*n*-butyrate 0.08

shows although the rate of the gas absorption decreased with a decrease in the reaction temperature. The yield of the ester increased at low temperatures; the total yields of the ester and aldehyde, based upon the amount of the gas absorbed, are about 70 or 80% at −30 and at −45 or −55°C respectively. The low yield of the ester at the relatively high reaction temperature seems to be partly due to the thermal instability of alkyl- and/or acylcobalt carbonyl.

From Fig. 3, it is evident that ethyl alcohol also has an acceleration effect in *n*-heptane. However, the effect seems to be about half of that for the reactions in toluene.

The effects of several organic compounds other than ethyl alcohol on this reaction at 0°C were examined; the results are summarized in Table II, in which the value of the gas absorption rate at the early stage of the reaction relative to the absorption rate in Exp. A is shown as a measure of the acceleration effect of the individual compound.

The results shown in Table II indicate that various kinds of organic compounds also have this effect, though their effects are considerably influenced by their structures. *n*- and *t*-butyl alcohols have an effects comparable to that of ethyl alcohol, but the effect of ethylene chlorohydrin is about one-twelfth that of ethyl alcohol. The compounds with functional groups other than an aliphatic hydroxy group, such as acetone, tetrahydrofuran, acetal, benzaldehyde, ethyl acetate and acetonitrile, also show the effect, but it is much smaller than that of ethyl alcohol. These facts seem to suggest that the compounds which have the effect are not limited to the above-mentioned compounds but may also include their homologues, i. e., alcohols, ketones, ethers, esters of carboxylic acids and nitriles.

The acceleration effect seems to be due to the basicity of these compounds. This consideration is supported by the following facts: phenol has no effect, and ethylene chlorohydrin, chloroacetone and acetylacetone have a smaller effect, than ethyl alcohol and acetone respectively. The chlorine atom and the acetyl group are considered to decrease the basicity of hydroxy and carbonyl groups with their nagative inductive effect.

The main product was ethyl β-hydroxy-*n*-butyrate in all of these cases. Even the reactions which were carried out in the presence of *n*- or *t*-butyl alcohol gave this ethyl ester*5 as a main product. This fact indicates that

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*5 Ethyl alcohol was used in the cleavage reaction with iodine.

TABLE III. THE REACTION OF STYRENE OXIDE WITH COBALT HYDROCARBONYL IN THE PRESENCE OF ETHYL (OR PROPYL) ALCOHOL

Exp. No.	Reaction condition*1			Alcohol added (mol./mol.-$HCo(CO)_4$)	CO absorbed (mol./mol.-$HCo(CO)_4$)	Product*2		
	Time min.	Mole ratio*3				Ester	α	β
						(mol./mol.-$HCo(CO)_4$)		
30	30	1.4	None	—	0	—	—	—
31	170	1.4	EtOH	2.0	0.72	—	—	—
32	120	1.2	EtOH	3.0	0.77	0.2	0.06	trace
33	160	1.2	PrOH	3.0	0.82	0.2	0.06	trace

*1 Other conditions: under one atmosphere of carbon monoxide and at −45°C

*2 Ester: α-phenyl-β-hydroxy- or β-phenyl-β-hydroxypropionate
α: α-phenylethyl alcohol β: β-phenylethyl alcohol

*3 Mole of styrene oxide per mole of cobalt hydrocarbonyl used

TABLE IV. THE REACTION OF EPICHLOROHYDRIN WITH COBALT HYDROCARBONYL IN THE PRESENCE OF ETHYL ALCOHOL

Exp. No.	Reaction condition*1		EtOH added (mol./mol.-$HCo(CO)_4$)	CO absorbed (mol./mol.-$HCo(CO)_4$)	Relative absorption rate*2	Product Ester*3 (mol./mol.-$HCo(CO)_4$)
	Time min.	Mole ratio				
34	225	1.5+1.5+1.5+1.5	3.0	0.82	—	0.55
35	60	14.5	0	0.10	—	—
36	180	14.5	1.0	0.61	1	0.4
37	150	14.5	2.0	0.86	2	0.6
38	85	14.5	8.0	0.93	10	0.6
39	100	5.8	8.0	0.81	4	0.55
40	70	5.8	12.0	0.97	6.5	0.6
41	160	2.9	8.0	0.82	2	0.55

*1 Other conditions: under one atmosphere of carbon monoxide and at 0°C

*2 The relative value of the gas absorption rate at the early stage of the reaction to the rate of Exp. 36

*3 Ethyl γ-chloro-β-hydroxy-*n*-butyrate

the alcoholysis of β-hydroxy-*n*-butyrylcobalt carbonyl did not occur in the course of the reaction. Thus, all of the additives appear to be acting as kinds of catalysts.

The Reactions of Styrene Oxide and Epichlorohydrin with Cobalt Hydrocarbonyl in the Presence of Ethyl Alcohol. — Styrene oxide was submitted to the reaction at −45°C; the results are summarized in Table III.

No gas absorption was observed in the reaction without ethyl alcohol under the conditions of Exp. 30, but a rapid gas absorption was observed in the presence of ethyl or propyl alcohol (Exp. 31—33), probably the carbonylation reaction was promoted by the addition of the alcohols. An ester-like compound was obtained as a main product after the cleavage of the reaction mixture with iodine and alcohol.*6 This ester may reasonably be considered to be β-phenyl-β-hydroxypropionate or α-phenyl-β-hydroxypropionate. As the minor by-products, α- and β-phenylethyl alcohols, which are the major products of the reaction without the alcohol at 0°C and at a relatively small mole ratio (1∼2),[2] were identified. These facts seem to support the supposition that the alcohol added accelerates the carbonylation reaction selectively. The low yield of the corbonylation product may be attributed to the instability of the corresponding acylcobalt carbonyl complex.

The results with epichlorohydrin are summarized in Table IV and in Fig. 4. The reactivity of epichlorohydrin is about several tenths that of propylene oxide;[2] at a relatively small mole ratio of epichlorohydrin (5∼6) no gas absorption was observed. Although the acceleration effect of the addition of alcohol has also been observed for the reaction of epichlorohydrin, the magnitude of this effect is smaller than those for propylene oxide and styrene oxide. The effect of the addition of ethyl alcohol was scarcely observed at a 1.5 mole ratio of epichlorohydin, even when 3 mol. of the alcohol, which is a sufficient amount in the reactions of propylene

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*6 The infrared spectrum of the products in toluene had a band at 1730 cm^{-1} corresponding to a carbonyl group. The retention time of the product (ester) in gas chromatography increased as the molecular weight of the alcohol used in the cleavage increased. The retention time of the ethyl ester was longer than that of ethyl hydrocinnamate.

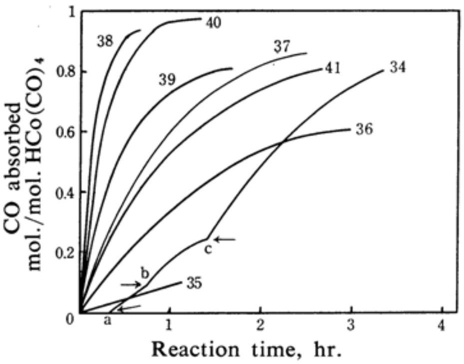

Fig. 4. CO absorption vs. time plots for the reactions of epichlorohydrin in the presence of ethyl alcohol.
a, b, and c: At these points, 1.5 mol. of epichlorohydrin per mole of $HCo(CO)_4$ was added.

oxide and styrene oxide, was added, but when additional amounts of epichlorohydrin were added successively, the acceleration of the gas absorption was clearly observed (Exp. 34 and and curve 34). At a 14.5 mol. ratio of epichlorohydrin at which a very slow gas absorption was observed without the alcohol (Exp. 35), a faster gas absorption evidently occurred when a larger amount of alcohol was added (Exp. 36—38).

The values of the gas absorption rate relative to the rate of Exp. 36 at an early stage of the reactions are shown in Table IV. At 14.5 and 5.8 mol. ratios, the rate increased proportionally with the increased amount of alcohol (Exp. 36—40). On the other hand, the rate increased with the increased amount of epichlorohydrin when the amount of the alcohol was fixed at 8.0 mol. (Exp. 38, 39 and 41). Thus, the rate of the gas absorption may be represented by the following equation:

$$\text{rate} = k\,[\text{epichlorohydrin}]\,[\text{ethyl alcohol}]$$

The main product of these reactions has been proved to be ethyl γ-chloro-β-hydroxy-*n*-butyrate from the considerations described previously.[2)] Thus, this carbonylation reaction is also promoted by the addition of alcohol.

In the reactions of propylene oxide or styrene oxide, however, the relationship given by the above equation was not observed. This observation may be interpreted in terms of the fact that propylene oxide and styrene oxide are much more reactive, in other words, the same relationship may exist under well-controlled reaction conditions, such as a lower reaction temperature and a smaller concentration.

In the light of the above equation, ethyl alcohol seems to form some complex with epichlorohydrin and/or cobalt hydrocarbonyl as the first step of the reaction; this complex is considered to be more reactive than epichlorohydrin and/or cobalt hydrocarbonyl.

The Hydroformylation of Ethylene Oxide in the Presence of Ethyl Alcohol.—The effect of the addition of ethyl alcohol on the hydroformylation of ethylene oxide has been examined.

Although ethylene oxide seems to undergo hydroformylation at 80～90°C, even without ethyl alcohol,[3)] only a little acrolein is obtained; some side reactions, such as isomerization, dehydration and polymerization may decrease the yield of the hydroformylation product considerably. By the addition of the alcohol (0.5～1.0 mol./mol.-ethylene oxide), however, the side reactions seemed to be considerably decreased, and then the hydroformylation product (β-hydroxypropionaldehyde[*7]) was obtained, though its yield was not good (at 80°C, about 15% of the amount of ethylene oxide used).

Summary

It has been observed that organic compounds with various kinds of functional groups have an accelerating effect on the reaction of olefin oxide with cobalt hydrocarbonyl and on the hydroformylation of olefin oxide.

1) The addition of a relatively small amount of ethyl alcohol promotes the carbonylation of propylene oxide with cobalt hydrocarbonyl until it is about 120 times faster than that of the standard run, carried out without alcohol. The amount of the alcohol necessary for this effect is about 2.0 mol./mol. $HCo(CO)_4$. As the reaction products, only compounds with a β-hydroxy-*n*-butyryl structure (ester and aldehyde) have been obtained.

2) The compounds other than ethyl alcohol, such as *n*- and *t*-butyl alcohol, ethylene chlorohydrin, acetone, tetrahydrofuran, ether, acetal, benzaldehyde, ethyl acetate and acetonitrile, also have the same effect on this reaction. Among these compounds, ethyl and butyl alcohols have the largest effect. On the other hand, phenol has no effect. The accelerating effect is considered to be due to the basicity of these compounds.

3) The reactions of styrene oxide and epichlorohydrin with cobalt hydrocarbonyl are also promoted by the addition of ethyl alcohol.

[*7] Identified by gas chromatography. 2, 4-Dinitrophenylhydrazone. Found: C, 45.7; H, 3.39; N, 24.8. Cald. for $C_9H_8O_4N_4$: C, 45.8; H, 3.38; N, 23.7%. M. p. 164～166°C. A mixed melting point with the hydrazone of authentic acrolein gave no depression. β-Hydroxypropionaldehyde is dehydrated to give acrolein in the formation of the hydrazone.

A relatively small amount of the alcohol accelerates selectively, the carbonylation of styrene oxide which is comparatively readily hydrogenated with cobalt hydrocarbonyl.²⁾ For epichlorohydrin, the following relationship was observed to exist at an early stage of the reaction: rate of the gas absorption $= k$ [epichlorohydrin] [ethyl alcohol].

4) The hydroformylation of ethylene oxide seems to be selectively promoted by the addition of ethyl alcohol, which gives β-hydroxypropionaldehyde, in a low yield.

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